

PHOSPHOR HANDBOOK

Edited under the Auspices of
Phosphor Research Society

Editorial Committee Co-chairs

Shigeo Shionoya

William M. Yen

Members

Takashi Hase

Shigeru Kamiya

Eiichiro Nakazawa

Kazuo Narita

Katsutoshi Ohno

Masaaki Tamatani

Marvin J. Weber

Hajime Yamamoto



CRC Press

Boca Raton Boston London New York Washington, D.C.

Acquiring Editor: Robert Stern
 Project Editor: Albert W. Starkweather, Jr.
 Cover design: Dawn Boyd

Library of Congress Cataloging-in-Publication Data

Phosphor handbook / edited under the auspices of the Phosphor Research Society ; editorial committee co-chairs Shigeo Shiono, William M. Yen ; members Takashi Hase ... [et al.]

p. cm.

Includes bibliographical references and index.

ISBN 0-8493-7560-6 (alk. paper)

1. Phosphors--Handbooks, manuals, etc. 2. Phosphors--Industrial applications--Handbooks, manuals, etc. I. Phosphor Research Society.

QC476.7.P48 1998

620.1'1295--dc21

98-15663

CIP

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage or retrieval system, without prior permission in writing from the publisher.

The consent of CRC Press LLC does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Specific permission must be obtained in writing from CRC Press LLC for such copying.

Direct all inquiries to CRC Press LLC, 2000 Corporate Blvd., N.W., Boca Raton, FL 33431.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are only used for identification and explanation, without intent to infringe.

© 1999 by CRC Press LLC (English language version)

© 1987 by the Phosphor Research Society (Keikotai Dogakkai) (Japanese language version)

Originally published in Japanese by Ohmsha, Ltd. under the title *Keikotai Handobukku*.

No claim to original U.S. Government works

International Standard Book Number 0-8493-7560-6

Library of Congress Card Number 98-15663

Printed in the United States of America 1 2 3 4 5 6 7 8 9 0

Printed on acid-free paper

Pr

This
Hand
was c
issue

T
in the
Form
in ph
opme
are p
and e
uted

T
have
with
prin
of th
chap
The r
Rese
the p
and
to th
their
deve
this

and
phor
role
this
and
will
Rese

Table 11 Phosphors for High-Pressure Mercury Lamps

Chemical composition	Luminescence color	Peak wavelength (nm)	Half-width (nm)	Application	Emission spectrum (Fig. No) ^a
YVO ₄ :Eu ³⁺	Red	619	5	Ordinary lamp	58
V(V,P)O ₄ :Eu ³⁺	Red	619	5	Ordinary lamp	58
(Sr,Mg) ₃ (PO ₄) ₂ :Sn ²⁺	Orange	620	40	Color improv. lamp	61
3.5MgO·0.5MgF ₂ ·GeO ₂ :Mn ²⁺	Deep red	655	15	Color improv. lamp	57
Y ₂ SiO ₅ :Ce ³⁺ ,Tb ³⁺	Green	543	—	Color improv. lamp	58
Y ₂ O ₃ ·Al ₂ O ₃ :Tb ³⁺	Green	545	—	Color improv. lamp	66
Y ₃ Al ₁₅ O ₁₂ :Ce ³⁺	Greenish-yellow	540	12	Low color temp. lamp	68
BaMg ₂ Al ₁₆ O ₂₇ :Eu ²⁺ ,Mn ²⁺	Blue-green	450, 515	—	Color improv. lamp	70
Sr ₂ Si ₃ O ₈ ·2SrCl ₂ :Eu ²⁺	Blue-green	490	7	Color improv. lamp	72
Sr ₁₀ (PO ₄) ₆ Cl ₂ :Eu ²⁺	Blue	447	32	Color improv. lamp	16
(Sr,Mg) ₂ (PO ₄) ₂ :Cu ²⁺	Blue-green	490	75	Color improv. lamp	74

^a See 5.6.3.

These phosphors are being used for fluorescent lamps that have high color rendering properties.

$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{F},\text{Cl})_2 \cdot \text{Sb}^{3+}, \text{Mn}^{2+}$

Crystal structure. These phosphors have a hexagonal structure and a crystal shape identical with natural apatite. The Ca atoms occupy two different sites: Ca atoms in Ca(I) sites are surrounded by six oxygen atoms and those in Ca(II) sites are contiguous with halogen atoms. In cases where the halogen is F, Ca(II) and F atoms are situated in the same crystal plane. When the halogen is Cl, however, Ca(II) cannot remain in the same crystal plane, due to the larger ionic radius of Cl.² The difference between these two configurations—namely, F-apatite and Cl-apatite—results in different luminescence properties. The configuration of (F,Cl)-apatite is the same as that of Cl-apatite. Although there are many reports concerning the sites of Sb and Mn, the consensus seems to be that these ions are capable of replacing Ca ions at both types of sites. While manganese ions are generally distributed rather uniformly in the crystal bulk, antimony ions are found mostly on the surface region of the crystal.³ Partial substitution of Ca by Sr is easy, and partial substitution by Ba or Cd is also possible. The Cd Cl-apatite belongs to another phosphor group.⁴

Emission characteristics. This phosphor series is typical of doubly activated phosphors. Energy transfer from Sb³⁺ to Mn²⁺ can be understood in terms of Dexter's resonance transfer theory. The Sb³⁺ emission peak in calcium halophosphate is located at ~480 nm at room temperature and is not influenced by the kind of halogen in the host. The emission peak of Mn²⁺ in calcium fluorophosphate is located at ~575 nm, whereas that of calcium chlorophosphate is located at ~585 nm. The manganese emission peak in calcium fluorochlorophosphate is located between these wavelengths, depending on the F:Cl ratio. Emission colors from blue-white to warm-white are easily obtained by choosing an appropriate Mn:Sb ratio. A typical example is shown in Figure 11; with increases in the Mn²⁺ concentration, the Mn²⁺ emission intensifies, while the Sb³⁺ emission is suppressed. When the Mn²⁺:Sb³⁺ ratio is 1, the peak intensity of the Mn²⁺ emission is 1.2 times that of the Sb³⁺ emission. The Sb³⁺ emission vanishes when the ratio rises above 3.3. The Mn²⁺ emission peak shifts to shorter wavelength when Ca is substituted by Sr.

At 83K, the Sb³⁺ emission is composed of a main emission band peaking at ~500 nm and a subband peaking at ~390 nm. With rising temperatures, the main emission band

ndbook

Chapter five: Phosphors for lamps

395

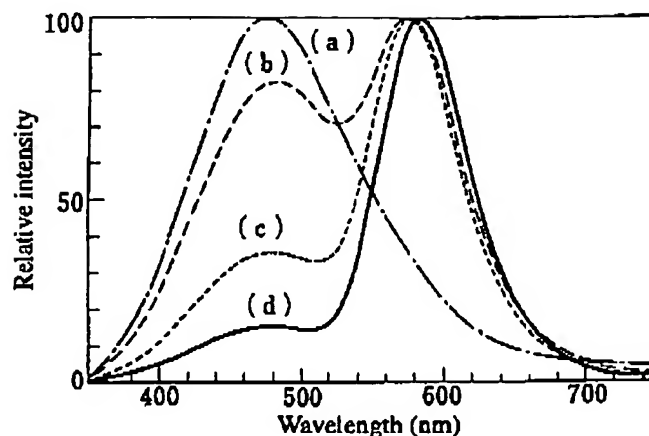
Emission
spectrum
Fig. No)58
58
61
57
58
66
68
70
72
16
74

Figure 11 Emission spectra of various calcium halophosphate phosphors activated by Sb^{3+} and Mn^{2+} : (a) blue-white $\text{Mn}^{2+}:\text{Sb}^{3+} = 0:0.15$ mol per 6PO_4 ; (b) daylight $\text{Mn}^{2+}:\text{Sb}^{3+} = 0.08:0.08$ mol per 6PO_4 ; (c) cool white $\text{Mn}^{2+}:\text{Sb}^{3+} = 0.17:0.08$ mol per 6PO_4 ; (d) warm white $\text{Mn}^{2+}:\text{Sb}^{3+} = 0.24:0.08$ mol per 6PO_4 . (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

dering

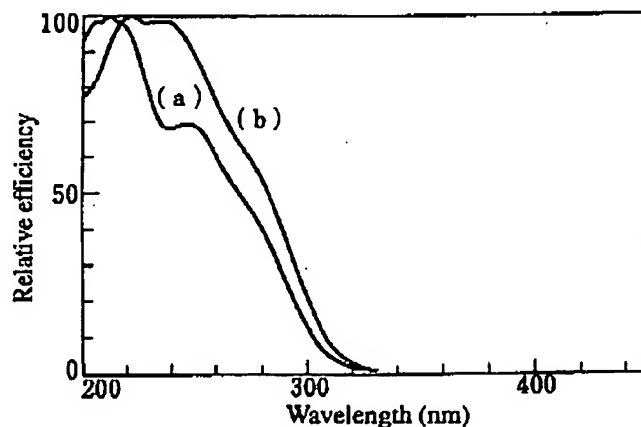
iden-
Ca(I)
s with
in the
same
e two
prop-
there
these
ns are
nostly
partial
phor

Figure 12 Excitation spectra of calcium halophosphate phosphor activated by Sb^{3+} and Mn^{2+} : (a) Sb^{3+} emission; (b) Mn^{2+} emission. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

phors.
nance
30 nm
The
s that
ak in
n the
osing
ses in
sup-
times
). The10 nm
band

shifts to shorter wavelength and becomes broader.⁵ The subband is not observed in the Sr halophosphate phosphor and its emission peak is located at ~500 nm at room temperature.⁶ Addition of Cd results in the shift of the Mn^{2+} emission to longer wavelength. As is clear from the excitation spectra shown in Figure 12, this phosphor series has good conformity with the 254-nm resonance radiation line generated in the low-pressure mercury discharge.

Temperature dependence. The manganese emission maintains relatively good characteristics at high temperatures. Almost 90% of the emission intensity is retained, even at 200°C, without a shift in the emission peak. The antimony emission band, however, shifts to shorter wavelengths with increasing ambient temperature. This results in a decrease of

the luminous efficacy.⁵ Therefore, the application of these phosphors for high-loading fluorescent lamps is limited.

Degradation characteristics. Halophosphate phosphors are relatively stable among all lamp phosphors in current use. However, an initial short-term degradation still exists. The degradation is caused by color center formation under irradiation with 185-nm UV radiation, which is a component in low-pressure mercury discharges.⁷⁻⁹ During the initial period of lamp operation, this phenomenon is pronounced. A brightness depression of 5 to 6% is observed within the first 10 minutes of lamp operation. After 1 hour of operation, the depression rate reaches 8 to 10%. The F-apatite phosphor has a lower depression rate than Cl- or (F,Cl)-apatite phosphors. With increases in the Sb concentration, the depression rate decreases. Partial replacement of Ca by Cd also results in remarkable diminution of the depression rate.⁸ Due to the fear of environmental contamination, however, this means of improvement has been abandoned. Besides the degradation caused by color center formation, the maintenance of light output during the lamp operation is strongly affected by lamp manufacturing conditions and by the kind of glass used in the envelope. The surface smoothness of the phosphors is another important factor that exerts influence on the maintenance of light output, as well as the efficacy of the lamps.

Preparation. CaHPO_4 , CaCO_3 , CaF_2 , CaCl_2 , Sb_2O_3 , and MnCO_3 are most commonly used as starting materials. The compounds NH_4F and NH_4Cl are also used to provide the halogen components. The preferred mixing ratio of these materials lies in a range that deviates from the stoichiometric value. A slight excess of PO_4 gives favorable results. The preferred range of the $\text{Me}:\text{PO}_4:\text{F,Cl}$ ratio lies between 9.8:6.0:1.6 and 9.95:6.0:1.9.¹⁰ These components are usually mixed by means of a dry system, such as ball mill and/or double corn mixer. Mixed materials are filled in crucibles or dishes and fired in an electric furnace at $\sim 1200^\circ\text{C}$ for several hours. The firing time depends on the quantity of material mixture in the vessel. The most important factor during the firing process is atmospheric control. Although atmospheric control can be attained using a reducing or inert gas flow, fine adjustment of the ventilation system is normally used for control. After crushing and milling the sintered cakes, the powdered phosphors are washed by acid or alkaline solution in order to make the crystal surface smooth. Removal of particles that are too fine is also essential for improved lamp efficacy as well as for better maintenance characteristics.^{11,12} For this reason, various means—either a dry or wet system utilizing sedimentation and centrifugation—are being employed. The control of crystal shape and particle size distribution of phosphors is quite important for practical lamp application. These phosphor characteristics strongly depend on those of the CaHPO_4 raw material.

Use. Phosphors containing both Sb^{3+} and Mn^{2+} are widely used for the standard warm-white, white, and daylight fluorescent lamps used for general lighting purposes. These phosphors are also utilized as the main component of the phosphor blend for Class A improved color rendering type lamps. Calcium halophosphate makes up the first layer in the double-layer construction of three-band fluorescent lamps.¹³ The phosphor activated by Sb^{3+} alone is used for blue-white color lamps and for color correction purposes of general lighting lamps.



Crystal structure. This phosphor belongs to the hexagonal Cl-apatite structure. Its lattice constant varies continuously, depending on the Ca:Ba ratio; the site occupied by Eu has not been determined.

Emission characteristics. The peak wavelength of emission changes with the Ca:Ba ratio. With increasing Ca content, the emission peak shifts to longer wavelengths and the emission

andbook

Chapter five: Phosphors for lamps

397

loading

ong all
sts. The
V radi-
: initial
ion of 5
eration,
ion rate
ression
tion of
: means
: center
affected
pe. The
ence on

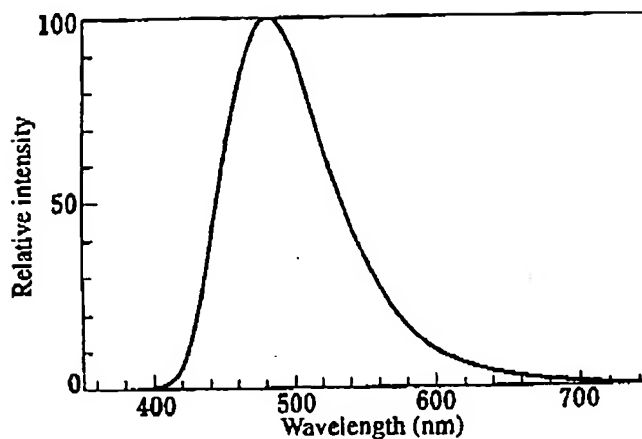


Figure 13 Emission spectrum of $(\text{Ba,Ca,Mg})_{10}(\text{PO}_4)_6\text{Cl}_2:\text{Eu}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

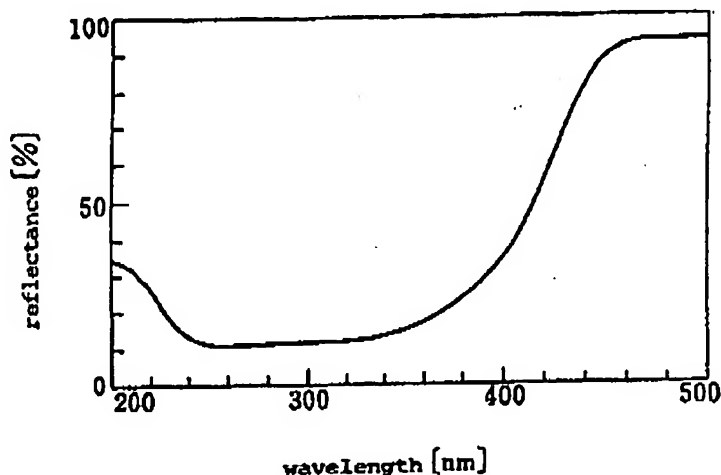


Figure 14 Spectral reflection of $(\text{Ba,Ca,Mg})_{10}(\text{PO}_4)_6\text{Cl}_2:\text{Eu}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

becomes broader. Partial replacement of Ca by Mg is effective in improving the efficacy as well as the maintenance. In Figure 13, the spectral power distribution of a typical example of this phosphor is shown. As is clear from the figure, the emission peak is located at ~ 483 nm and the spectrum is asymmetrical. Whereas a steep emission energy decrease is observed in the shorter wavelength side, the emission in the longer wavelength side is gently sloping and extends beyond 600 nm. The absorption band of these phosphors is well into the blue region of the spectrum, as is clear from the spectral reflection curves shown in Figure 14. This property is useful in suppressing the intensity of mercury lines in the blue region, resulting in improvement of the color rendering property of fluorescent lamps. The excitation spectrum also extends into the blue region, as is shown in Figure 15.

s lattice
Eu has

ia ratio.
mission

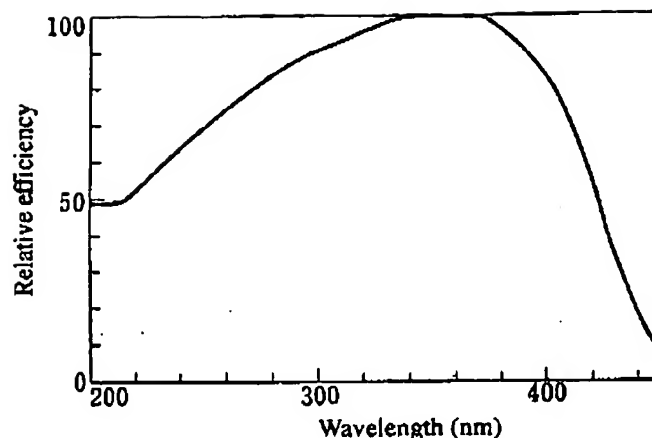


Figure 15 Excitation spectrum of $(\text{Ba,Ca,Mg})_{10}(\text{PO}_4)_6\text{Cl}_2:\text{Eu}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

Preparation. A mixture of BaHPO_4 , BaCO_3 , CaCO_3 , MgO , NH_4Cl , and Eu_2O_3 is fired at 800 to 1000°C in air for several hours. After milling and sieving the sintered cake, a second firing is carried out at the same temperature as the first in a slightly reducing atmosphere for several hours. The stoichiometric composition ratio of the total metal components to phosphoric acid gives optimal results. When the Ca content is 1 mole:6 PO_4 and that of Mg is 0.1 mole:6 PO_4 , the emission peak is located at 467 nm. With increasing Ca content, the emission peak shifts to longer wavelengths and reaches 497 nm when the Ca content is 3 mole:6 PO_4 . The Eu concentration to obtain the highest efficacy is around 0.2 mole:6 PO_4 . The preferable Mg content lies in the 0.1–0.2 mole:6 PO_4 range.

Use. The blend of this phosphor with a $(\text{Sr,Mg})_3(\text{PO}_4)_2:\text{Sn}^{2+}$ phosphor makes it possible to construct the fluorescent lamps with high color rendering Class AAA, even when a simple single-layer coating is employed.

$\text{Sr}_{10}(\text{PO}_4)_6\text{Cl}_2:\text{Eu}^{2+}$ and $(\text{Sr,Ca,Ba})_{10}(\text{PO}_4)_6\text{Cl}_2:\text{Eu}^{2+}$

Crystal structure. Among the alkaline earth halophosphate crystals, only Cl-apatite gives efficient emission by activation with divalent europium. The lattice constant and spectral power distributions are dependent on the ratio of the metal species.¹⁵

Emission characteristics. The Eu^{2+} -activated Sr Cl-apatite gives a sharp emission spectrum peaking at 447 nm, as shown in Figure 16(a).¹⁶ Partial replacement of Sr by Ca results in the shift of the emission peak to longer wavelength, and the emission spectrum becomes asymmetric in the long-wavelength region. The emission peak shifts to 452 nm when 1 mole Sr is replaced by Ca, as shown in Figure 16(b). Although the replacement of Sr by Ba is supposed to result in the shift of the emission peak to shorter wavelengths, a systematic study of the Sr-Ba system has not been made. When 1 mole each Ca and Ba replace Sr, the emission peak wavelength is found at 445 nm. Incorporation of a small amount of Ba serves to improve the degradation characteristics of the phosphor.¹⁵ It is also reported that an increase in the emission intensity is observed when a small amount of phosphate is replaced by borate.¹⁵ The excitation spectrum is also affected by the composition of the matrix, especially in the wavelength region shorter than 300 nm. In Figure 17, the excitation spectra of a typical Sr-Ca Cl-apatite

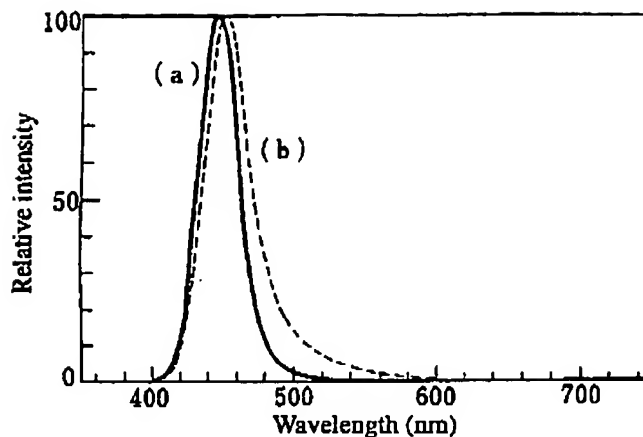


Figure 16 Emission spectra of $(\text{Sr},\text{M})_{10}(\text{PO}_4)_6\text{Cl}_2:\text{Eu}^{2+}$: (a) $M = 0$; (b) $M = 0.1 \text{ Ca}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

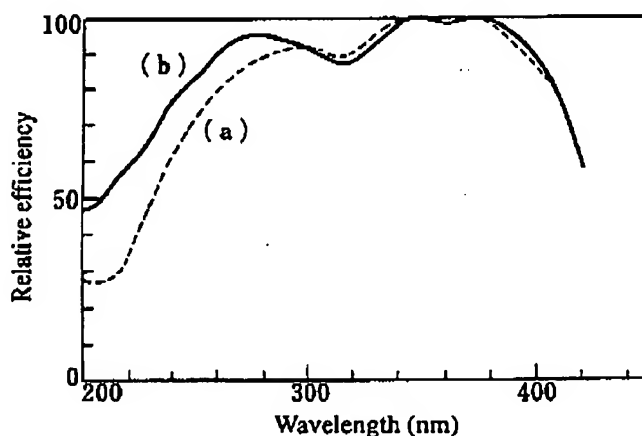


Figure 17 Excitation spectra of $(\text{Sr},\text{Ca})_{10}(\text{PO}_4)_6\text{Cl}_2:\text{Eu}^{2+}$: (a) without B_2O_3 ; (b) with B_2O_3 . (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

with and without borate incorporation are shown. This series of phosphors has a broad excitation band resulting in good response to both short- and long-wavelength UV excitation.

Preparation. A mixture of raw materials, such as SrHPO_4 , SrCO_3 , SrCl_2 , CaCl_2 , BaCl_2 , and Eu_2O_3 , in the desired ratio, is fired at 1000 to 1200°C in a slightly reducing atmosphere. The sintered cake is converted to the powder in the usual way. The ratio of the total metal components to the sum of the phosphate and borate combined is adjusted, preferably to the stoichiometric value. The appropriate Eu concentration used is around 0.03 mole:6 PO_4 .

Use. These phosphors are mainly used for the blue color component of three-band fluorescent lamps.

5.6.2.2 Phosphate phosphors

Phosphate compounds have been utilized as host materials of lamp phosphors for many years, thanks to their relatively low material cost, easy synthesis, and reasonable stability in lamp application. The development of the first synthesized alkaline earth phosphate phosphor can be traced back to 1938. In the 1960s, rare-earth-activated alkaline earth phosphate phosphors were practically used in photocopying fluorescent lamps. This was the first application of rare-earth-activated phosphors in fluorescent lamps and represented a landmark in the history of fluorescent lamp development.

Recently, rare-earth-activated, green-emitting phosphate phosphors have successively been developed for three-band lamps as competitive materials to aluminate phosphors.

Phosphates are still being explored as one of the promising matrix crystals for new lamp phosphor development.

$\text{Sr}_2\text{P}_2\text{O}_7:\text{Sn}^{2+}$

Crystal structure. The $\text{Sr}_2\text{P}_2\text{O}_7$ crystal is dimorphic. A high-temperature treatment results in the α phase crystal, whereas the β phase is formed at low temperature. The practical phosphor belongs to the α type.

Emission characteristics. The emission color of alkaline earth pyrophosphates activated by divalent tin varies from blue to green depending on the species of the alkaline earth metal.¹⁷⁻¹⁹ The Sr pyrophosphate phosphor has a relatively broad emission band peaking at 464 nm, as shown in Figure 18. The color coordinate of the emission is calculated to be $x = 0.160$, $y = 0.179$. The excitation spectrum of this phosphor is shown in Figure 19. In addition to efficient excitation by UV radiation of wavelength shorter than 300 nm, this phosphor can also be excited by electron beam or by X-ray.

Preparation. Raw materials are ordinarily chosen from SrHPO_4 , SrCO_3 , $(\text{NH}_4)_2\text{HPO}_4$, and SnO . To preserve the divalent state of tin, a slightly reducing atmosphere is required during the firing process. Preferable firing temperatures are ~ 900 to 1000°C . The amount of Sn is in the vicinity of 1 to 2 mol%.

Use. This phosphor was occasionally utilized to improve the color rendering property of fluorescent lamps.

$(\text{Sr,Mg})_3(\text{PO}_4)_2:\text{Sn}^{2+}$

Crystal structure^{21,22} When pure $\text{Sr}_3(\text{PO}_4)_2$ is heated to between 1000 and 1600°C and then rapidly cooled down to room temperature, a rhombohedral structure is obtained. Above 1305°C , transition into a structure similar to $\beta\text{-Ca}_3(\text{PO}_4)_2$ has been identified by differential thermal analysis. This means that the crystal structure of pure $\text{Sr}_3(\text{PO}_4)_2$ is always rhombohedral at room temperature, independent of the synthesis temperature. However, partial replacement of Sr, either by Mg, Ca, Zn, or Cd, makes it possible to keep the $\beta\text{-Ca}_3(\text{PO}_4)_2$ structure even at room temperature. Only the β type phosphate gives efficient fluorescence.

Emission characteristics. Mg in too large an amount gives a strongly sintered phosphor cake, resulting in low emission intensity. The highest brightness is obtained in the β -type structure but only at a critical composition close to the border where α and β -type structures co-exist.²² As shown in Figure 20, this phosphor has a broad emission band with a peak at 620 nm. The highest quantum efficiency is obtained when 11 mol% $\text{Sr}_3(\text{PO}_4)_2$ is replaced by $\text{Mg}_3(\text{PO}_4)_2$. In this case, the efficiency reaches 0.96. Such high efficiency is not observed in the Ca or Cd compounds. When the Sr-Mg phosphate is used, the luminous efficacy of a 40-W fluorescent lamp is as high as 56 lm W^{-1} . The excitation spectrum shown in Figure 21 illustrates clearly that this phosphor is also efficiently excited by the 365-nm

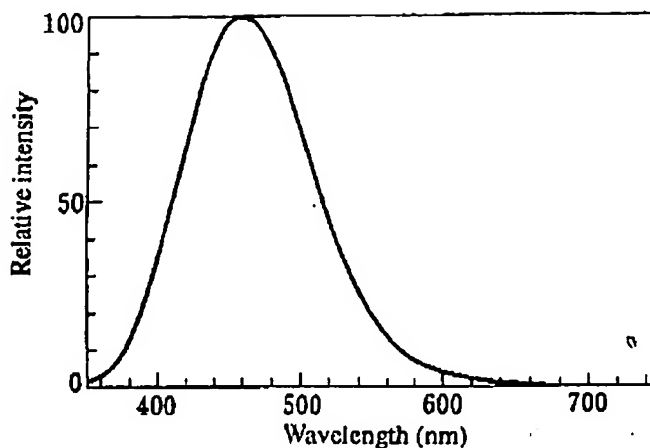


Figure 18 Emission spectrum of $\text{Sr}_2\text{P}_2\text{O}_7:\text{Sn}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

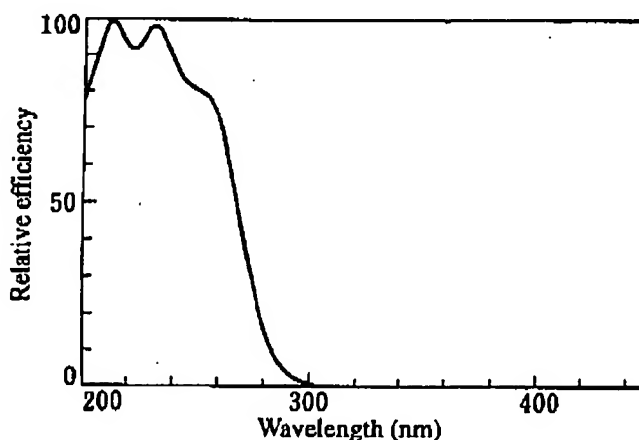


Figure 19 Excitation spectrum of $\text{Sr}_2\text{P}_2\text{O}_7:\text{Sn}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

radiation generated in the high-pressure mercury discharge. Thanks to this excitation characteristic and the excellent high-temperature characteristics, this phosphor has been widely used for the purposes of color correction and efficacy improvement in high-pressure mercury lamps.

Preparation. SrHPO_4 , SrCO_3 , $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, and SnO are commonly used as raw materials. The preferred Sn concentration is 2 to 4 mol%. Firing is carried out at 1000 to 1200°C in a slightly reducing atmosphere for several hours. Special caution must be taken for atmospheric control to preserve Sn in the divalent state during the firing process. The sintered cake is milled to a powder by ordinary means.

Use. This phosphor is very important as the red-emitting component of extremely high color rendering fluorescent lamps of Class AAA.

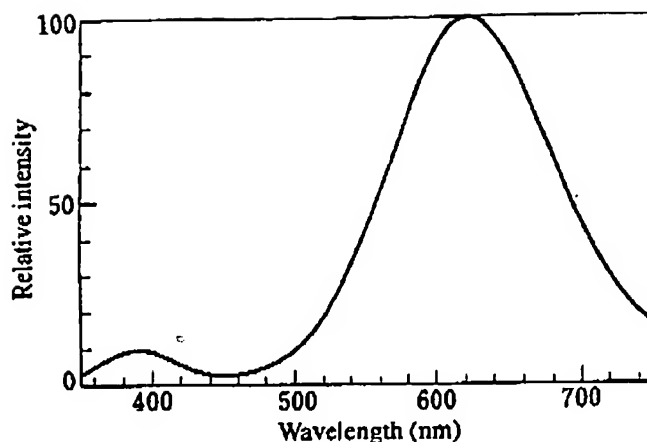


Figure 20 Emission spectrum of $(\text{Sr,Mg})_3(\text{PO}_4)_2:\text{Sn}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

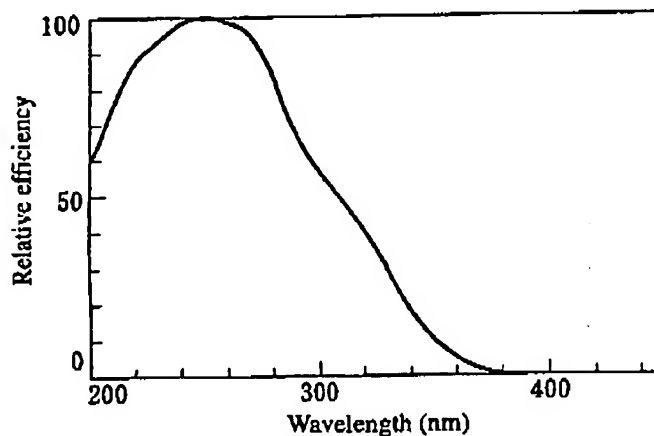


Figure 21 Excitation spectrum of $(\text{Sr,Mg})_3(\text{PO}_4)_2:\text{Sn}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

$(\text{Ca,Zn})_3(\text{PO}_4)_2:\text{Ti}^+$

Crystal structure. The $\text{Ca}_3(\text{PO}_4)_2$ crystal is dimorphous. The α phase forms at temperatures higher than 1180°C and the β phase crystal forms below that temperature. For practical lamp phosphors, Ca-Zn orthophosphate has been used as the matrix composition in order to shift emission peaks for a particular application.

Emission characteristics. The emission peak of $\text{Ca}_3(\text{PO}_4)_2:\text{Ti}^+$ is located at 328 nm, as shown in Figure 22(a).²³ This peak wavelength deviates from the erythematic sensitivity peak of 298 nm. Shifting of the emission peak is possible by partial replacement of Ca by Zn. With an increase in the Zn amount, the emission peak shifts to shorter wavelengths. The composition in practical use is $(\text{Ca}_{0.9}\text{Zn}_{0.1})_3(\text{PO}_4)_2:\text{Ti}^+$, with emission peak located at 310 nm, i.e., nearer to the erythematic sensitivity peak, as shown in Figure 22(b).²⁴ Partial replacement of Ca by Zn does not alter the excitation spectrum significantly, as shown in

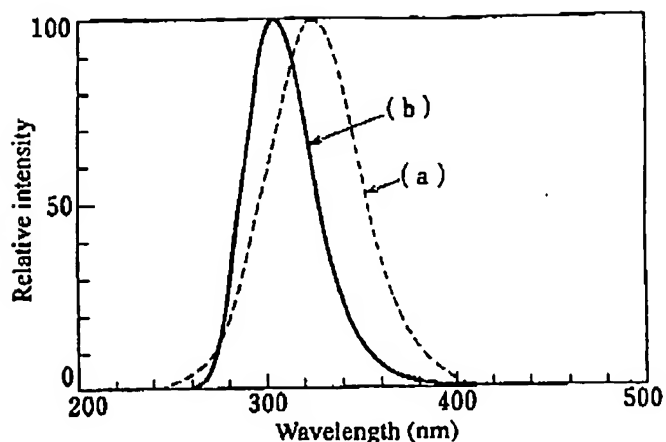


Figure 22 Emission spectra of (a) $\text{Ca}_3(\text{PO}_4)_2:\text{Tl}^+$ and (b) $(\text{Ca,Zn})_3(\text{PO}_4)_2:\text{Tl}^+$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

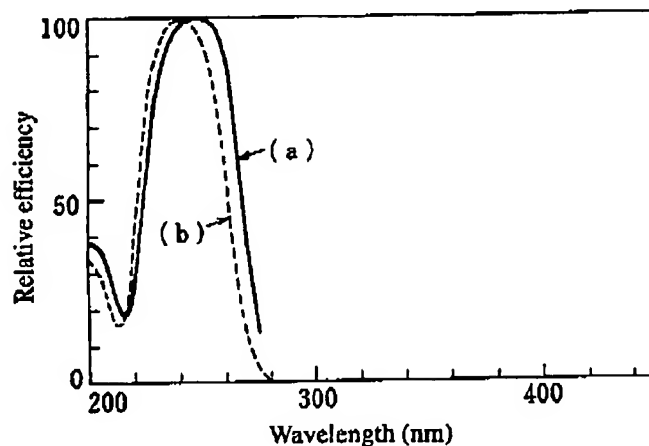


Figure 23 Excitation spectra of (a) $\text{Ca}_3(\text{PO}_4)_2:\text{Tl}^+$ and (b) $(\text{Ca,Zn})_3(\text{PO}_4)_2:\text{Tl}^+$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

Figure 23. 40-W fluorescent lamps employing this phosphor generate 7.5 to 8.0 W of UV radiation with an output of 1.3 to 1.75 W at the erythemal wavelength.

Preparation. Usually, CaHPO_4 , CaCO_3 , ZnO , and TiNO_3 are used as starting materials. The blended materials are then fired at 900 to 1000°C in air. A favorable result is obtained by firing at relatively low temperatures because this minimizes the evaporation loss of Tl. The optimal Tl concentration is ~3 to 4 mol%.

Use. This phosphor is exclusively utilized for fluorescent sun lamps.



Crystal structure. The crystal structure of these phosphors have been identified as orthorhombic α type. The lattice constants of $\text{Sr}_2\text{P}_2\text{O}_7$ are $a = 8.98 \text{ \AA}$, $b = 13.13 \text{ \AA}$, and $c = 5.40 \text{ \AA}$.

Emission characteristics. Because the divalent Eu ion emission originates from an electric dipole transition between the $4f^65d$ and $4f^7$ configurations, its emission spectrum is relatively broad and the spectrum is influenced strongly by the matrix structure.²⁶⁻²⁸ According to X-ray analysis, Sr-Mg pyrophosphate has a different structure from either Sr or Mg pyrophosphates. The emission peak of $(\text{Sr,Mg})_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$ is located at 394 nm, whereas that of $\text{Sr}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$ is located at 420 nm, as shown in Figure 24(a) and (b), respectively. As shown in Figure 25, the excitation spectra of both phosphors extend to the long-wavelength UV region. High excitation probability of these phosphors at 254 nm explains their suitability for fluorescent lamp application. The quantum efficiency of the optimized phosphors under 250- to 270-nm excitation reaches 0.95. The temperature dependence of the efficiency of these phosphors is somewhat inferior to that of $\text{Sr}_3(\text{PO}_4)_2\text{:Eu}^{2+}$ discussed below. The quenching temperature of the emission is $\sim 200^\circ\text{C}$.

Preparation. SrHPO_4 , MgNH_4PO_4 , and Eu_2O_3 are commonly used as raw materials. Firing is made at 1000 to 1200°C in a slightly reducing atmosphere for several hours. Preferred Eu concentrations are ~ 2 mol%.

Use. These phosphors are used for fluorescent lamps in photochemical application; particular use is in photocopying lamps for diazo-sensitive paper systems.

$\text{Sr}_3(\text{PO}_4)_2\text{:Eu}^{2+}$

Crystal structure^{27,28}. The crystal phase of $\text{Sr}_3(\text{PO}_4)_2$ changes from α to β or β to α type at 1305°C . This transition temperature decreases by 125 to 150°C when Eu^{2+} ions are incorporated. Crystals heated to temperatures higher than 1000°C and then cooled rapidly show the α phase. This procedure assumes that the crystal phase of this phosphor is always of the α type, independent of firing temperature. The emission intensity, however, depends strongly on the firing temperature. A high brightness phosphor is obtained only by high-temperature firing where β type formation takes place prior to temperature quenching.

Emission characteristics. The emission peak of this phosphor is located at 408 nm, as shown in Figure 24(c). When the Sr is partially replaced by either Mg, Ca, Zn, or Cd, β type structures are obtainable even at room temperature. The emission intensity of Eu^{2+} -activated phosphors employing these materials as hosts is insufficient for practical application.²⁸ The peak height of $\text{Sr}_3(\text{PO}_4)_2\text{:Eu}^{2+}$ is only about 70% that of $\text{Sr}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$ at room temperature; however, this situation is reversed at high temperatures.²⁹ In addition, the excitation spectrum of this phosphor is different from those of the pyrophosphate phosphors. As shown in Figure 25(c), two separate bands are clearly observable in the excitation spectrum.

Preparation. A mixture of SrHPO_4 , SrCO_3 , and Eu_2O_3 is commonly employed as the starting material. Firing is made at 1200 to 1250°C in a slightly reducing atmosphere for several hours. Addition of a small excess of Sr yields improved results. The appropriate Eu concentration is ~ 2 mole.

Use. These phosphors are used for fluorescent lamps in photochemical applications, particularly photocopying using diazo-sensitive paper systems.

$2\text{SrO}\cdot 0.84\text{P}_2\text{O}_5\cdot 0.16\text{B}_2\text{O}_3\text{:Eu}^{2+}$ ³⁰

Crystal structure. This phosphor matrix is obtained by partial replacement of P_2O_5 by B_2O_3 in $\text{Sr}_2\text{P}_2\text{O}_7$. X-ray analysis, however, shows that the crystal structures of these two materials are different from each other.

Emission characteristics. This phosphor gives a blue-green emission whose peak is located at 480 nm, as shown in Figure 26. This phosphor is efficiently excited not only by 254-nm radiation, but also by the 405- and 436-nm mercury lines owing to its broad excitation

Handbook

Chapter five: Phosphors for lamps

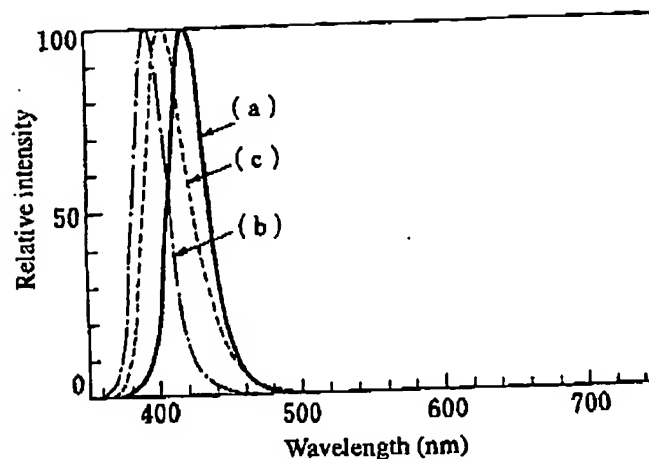


Figure 24 Emission spectra of (a) $\text{Sr}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$; (b) $(\text{Sr,Mg})_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$; and (c) $\text{Sr}_3(\text{PO}_4)_2\text{:Eu}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

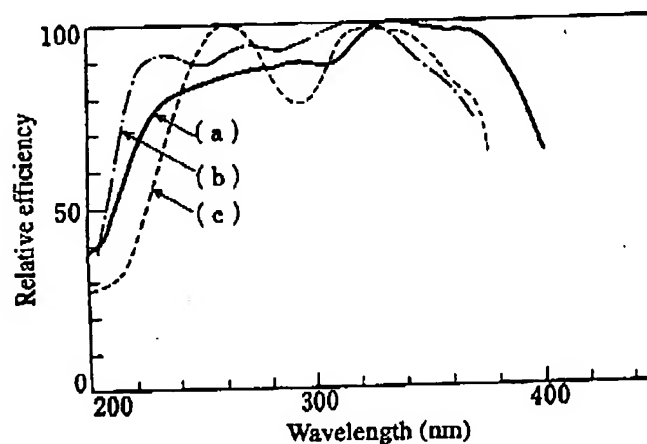


Figure 25 Excitation spectra of (a) $\text{Sr}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$; (b) $(\text{Sr,Mg})_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$; and (c) $\text{Sr}_3(\text{PO}_4)_2\text{:Eu}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

spectrum; the latter extends from the UV all the way into the visible, as shown in Figure 27. The luminous efficacy of 62 lm W^{-1} when used in a 40-W fluorescent lamp is higher than that of the calcium halophosphate phosphor activated with trivalent antimony.

Preparation. The starting materials are SrHPO_4 , SrCO_3 , H_3BO_3 (99.5%), and Eu_2O_3 . Firing is made at 1100 to 1250°C in a slightly reducing atmosphere for several hours. Eu concentrations of 2 to 3 mol% are normally used.

Use. This phosphor is utilized for Class AAA high color rendering fluorescent lamps as its blue/green-emitting component. The absorption spectrum extending to the blue color region has the advantage of suppressing the mercury emission lines in the blue region, which normally influence the color rendering property of fluorescent lamps unfavorably. Proper combination of this phosphor with an orange-emitting phosphor makes it possible

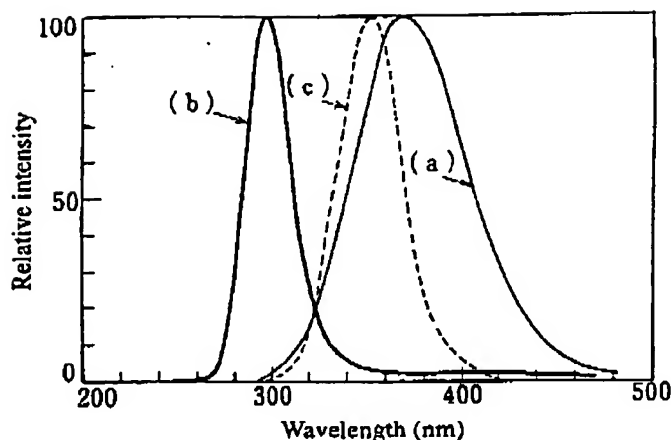


Figure 34 Emission spectra of (a) $(\text{Sr}, \text{Ba}, \text{Mg})_3\text{Si}_2\text{O}_7:\text{Pb}^{2+}$; (b) $(\text{Ba}, \text{Zn}, \text{Mg})_3\text{Si}_2\text{O}_7:\text{Pb}^{2+}$; and (c) $\text{BaSi}_2\text{O}_7:\text{Pb}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

excitation spectra of the $\text{Sr}_{0.6}\text{Ba}_{1.4}\text{MgSi}_2\text{O}_7:\text{Pb}^{2+}$ phosphor are shown in Figure 34(a) and 35(b), respectively.

Preparation. A slurry is made of SrCO_3 , BaCO_3 , MgCO_3 , and SiO_2 in the mole ratio 0.6:1.4:1.0:2.0 with water. Some 3% of a Pb compound, usually $\text{Pb}(\text{NO}_3)_2$ in an aqueous solution, is added to the mixture. The paste is dried and milled. The resulting powder is fired at $\sim 1050^\circ\text{C}$ in air for several hours.

Use. The phosphor had been used in diazo copying lamps until the $\text{SrP}_2\text{O}_7:\text{Eu}^{2+}$ phosphor was introduced. Currently, it is used in lamps for photochemical and insect-catching purposes.

$(\text{Ba}, \text{Zn}, \text{Mg})_3\text{Si}_2\text{O}_7:\text{Pb}^{2+}$

Crystal structure. The fluorescence and the phase diagrams of the Pb^{2+} -activated $\text{BaO}-\text{MgO}-\text{SiO}_2$ and $\text{BaO}-\text{ZnO}-\text{SiO}_2$ systems have been reported. Both $\text{BaMg}_2\text{Si}_2\text{O}_7$ and $\text{BaZn}_2\text{Si}_2\text{O}_7$ have been identified by X-ray analysis as having single phases. The similarity between these two phosphors indicates that they are isomorphous; it has been also confirmed that these compounds can make a solid solution. Thermal analysis indicates that $(\text{Ba}, \text{Zn})_3\text{Si}_2\text{O}_7$ has a reversible crystallographic transition at about 270°C . Due to this transition, this phosphor detaches easily from the tube wall during fluorescent lamp production. However, the transition disappears when more than 0.05 mole Zn^{2+} is replaced by Mg^{2+} . Thus, practical usable phosphors employ the composition $\text{BaZn}_{1.9}\text{Mg}_{0.1}\text{Si}_2\text{O}_7:\text{Pb}^{2+}$.

Emission characteristics. The emission peak of $\text{BaZn}_2\text{Si}_2\text{O}_7:\text{Pb}^{2+}$ phosphor is located at 303 nm, whereas that of the $\text{BaMg}_2\text{Si}_2\text{O}_7:\text{Pb}^{2+}$ phosphor is at 290 nm. The emission intensity of the latter is lower than that of the former. These two phosphors form solid solutions with emission peak position depending on the Mg:Zn ratio. The emission peak shifts to shorter wavelengths with increases in the Mg^{2+} content. The emission intensity decreases when more than 20% of the Zn^{2+} is replaced by Mg^{2+} ; however, at low replacement levels, an increase in the emission intensity is observed. As the intensity decreases, another emission band (370-nm peak) appears. The emission peak of the practical phosphor $\text{BaZn}_{1.9}\text{Mg}_{0.1}\text{Si}_2\text{O}_7:\text{Pb}^{2+}$ is located at 295 nm, as shown in Figure 34(b). Its excitation spectrum is shown in Figure 35(b).

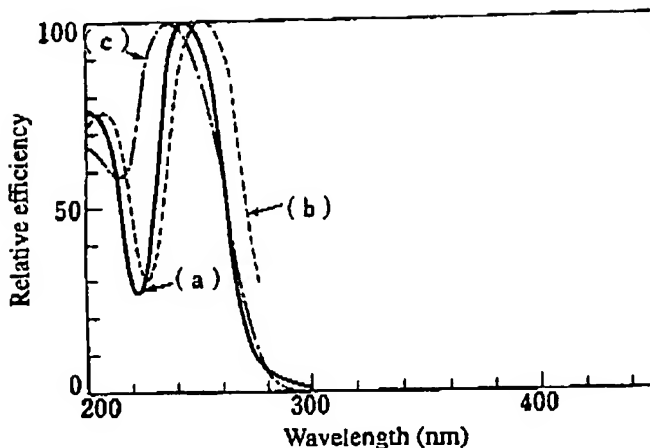


Figure 35 Excitation spectra of (a) $(\text{Sr}, \text{Ba}, \text{Mg})_3\text{Si}_2\text{O}_7:\text{Pb}^{2+}$; (b) $(\text{Ba}, \text{Zn}, \text{Mg})_3\text{Si}_2\text{O}_7:\text{Pb}^{2+}$; and (c) $\text{BaSi}_2\text{O}_5:\text{Pb}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

Preparation. A slurry is made of BaCO_3 , ZnO , MgO , and SiO_2 with water. The mixing ratio of BaCO_3 is made lower than the stoichiometric ratio, $\text{BaO} \cdot 1.92\text{ZnO} \cdot 0.1\text{MgO} \cdot \text{SiO}_2$; 1 mol% of Pb^{2+} , usually as $\text{Pb}(\text{NO}_3)_2$ in an aqueous solution, is added to the blend. The paste is dried and milled. The resulting powder is fired at 1100 to 1200°C in air for several hours.

Use. This phosphor was used for fluorescent sun lamps. This application, however, has been taken over by the $(\text{Ca}, \text{Zn})_3(\text{PO}_4)_2:\text{Ti}^+$ phosphor due to relatively poor maintenance characteristics.

$\text{BaSi}_2\text{O}_5:\text{Pb}^{2+}$ ^{41,42}

Crystal structure. The $\text{BaSi}_2\text{O}_5:\text{Pb}^{2+}$ phosphor is isomorphous with the mineral sanbornite and has rhombic symmetry.

Emission characteristics. The $\text{BaSi}_2\text{O}_5:\text{Pb}^{2+}$ phosphor shows a strong UV emission peaked at 350 nm under 253.7-nm excitation. The emission and excitation spectra are shown in Figures 34(c) and 35(c), respectively.

Preparation. The starting materials are SiO_2 and BaCO_3 . The highest brightness is obtained when 5 mol% SiO_2 in excess of the stoichiometric ratio is blended; 3 mol% Pb^{2+} , usually $\text{Pb}(\text{NO}_3)_2$ in an aqueous solution, is also added. The mixed paste is dried and milled. The resulting powder is fired in air at 1100 to 1250°C for a few hours.

Use. This phosphor is used for black-light lamps.

$\text{Sr}_2\text{Si}_3\text{O}_8 \cdot 2\text{SrCl}_2:\text{Eu}^{2+}$

Crystal structure. The Eu^{2+} -activated alkaline earth halosilicate phosphors were invented by Leete and Mckeag.⁴³ X-ray analysis shows that this phosphor has a novel crystal structure that is different from that of other Sr silicates. Detailed luminescence characteristics have been reported.⁴⁴ However, a definitive crystal structure for these materials has not been established.

Emission characteristics. This phosphor emits blue-green luminescence and its emission peak is located at 490 nm, as shown in Figure 36(a). Besides this main emission band, an

additional band peaking at 425 nm due to $\text{SrCl}_2:\text{Eu}^{2+}$ occasionally appears in the sintered product. This emission band can be removed by washing with water.⁴⁵ The excitation spectrum of this phosphor is shown in Figure 37(a). The luminescence mechanism of this phosphor can be explained by the $4f^7-4f^65d$ excitation and emission model for Eu^{2+} . Owing to the splitting of d states, the excitation spectrum shows a broad band extending from 200 to 450 nm. This phosphor has good temperature characteristics under 365-nm excitation; the brightness at 330°C retains 50% of its room-temperature value.

Preparation. The starting materials— SrCO_3 , SiO_2 , and SrCl_2 in the ratio of 2:3:2 with 0.01 Eu_2O_3 —are mixed with pure water. The paste is dried at 120°C and pre-fired at 850°C for 3 hours. The pre-fired cake is milled and then re-fired for a few hours at 950°C in a slightly reducing atmosphere of nitrogen containing 2% hydrogen by volume. The sintered product is cooled in this atmosphere and milled to a powder. Finally, the powder is washed with water to remove the remaining SrCl_2 .

Use. This phosphor was considered as the blue-green component for high color rendering fluorescent lamps, but was not widely used due to shortfalls in its maintenance characteristics. The phosphor is currently employed for color correction of high-pressure mercury lamps because of its high temperature properties.

$\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$

Crystal structure. The crystal structure of the $\text{Me}_3(\text{Me}=\text{Ca}, \text{Sr}, \text{Ba})\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ phosphor is isomorphous with the mineral merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$), which has rhombic symmetry.⁴⁰

Emission characteristics. The emission spectra of the $\text{Me}_3(\text{Me}=\text{Ca}, \text{Sr}, \text{Ba})\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ phosphor depend on the species of alkaline earth metal used in the compound. The emission peak of the phosphor containing Ca is located at 475 nm, and those of the phosphors containing Sr or Ba are located at 460 and 440 nm, respectively.⁴⁶ The emission spectrum of the $\text{BaMgSi}_2\text{O}_8:\text{Eu}^{2+}$ phosphor is shown in Figure 36(b). The phosphor has a quantum efficiency of 0.50 under the 250–270-nm excitation. As is clear from Figure 37(b), the excitation spectrum of this phosphor extends from 200 to 460 nm. Therefore, this phosphor can be excited even by blue light.

Temperature dependence. The temperature dependence of the emission intensity of $\text{Me}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ ($\text{Me}=\text{Ca}, \text{Sr}, \text{Ba}$) phosphors depends on the alkaline earth species involved. Corresponding to the change of Me, going from Ca to Sr or to Ba, temperature characteristics become better. The emission intensity of $\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ at 270°C is about 50% of that observed at room temperature.

Preparation. The raw materials— BaCO_3 , MgCO_3 , and very fine SiO_2 —are mixed in the mole ratio 3:1:2 with 0.01 mole Eu_2O_3 . The mixture is fired at 1100 to 1300°C for a few hours in a slightly reducing atmosphere, preferably a mixture of 5 volume percent hydrogen in nitrogen. The sintered product is cooled in this atmosphere.

Use. Since the $\text{Ba}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$ phosphor has a narrow blue emission band, it is used for color correction purposes. The phosphor co-activated with Mn^{2+} has the characteristic manganese orange emission band peaking at 620 nm in addition to the Eu^{2+} 443-nm band. This phosphor finds its application in plant growth lamps.⁴⁷

$(\text{Sr}, \text{Ba})\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$

Crystal structure. Feldspar is the general classification for the mineral structure containing the three-dimensional silicon-aluminum-oxygen framework. The frameworks of all the alkaline earth feldspars are the same. The crystal symmetries, however, are different, depending on the size of the species involved. The Sr-feldspar ($\text{SrAl}_2\text{Si}_2\text{O}_8$) has triclinic

Handbook

Chapter five: Phosphors for lamps

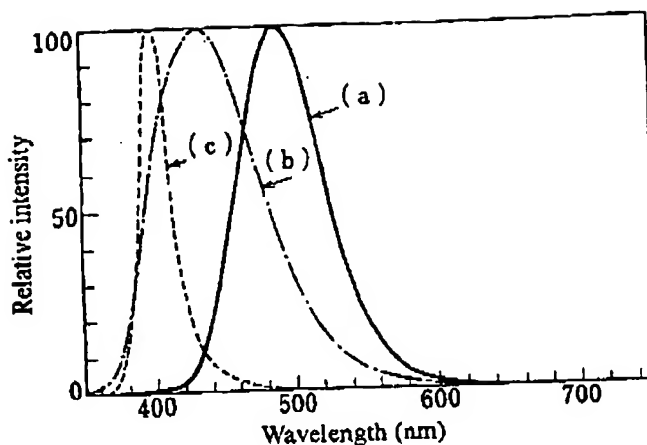


Figure 36 Emission spectra of (a) $\text{Sr}_2\text{Si}_3\text{O}_8 \cdot 2\text{SrCl}_2 \cdot \text{Eu}^{2+}$; (b) $\text{Ba}_3\text{MgSi}_2\text{O}_8 \cdot \text{Eu}^{2+}$; and (c) $(\text{Sr},\text{Ba})\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{Eu}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

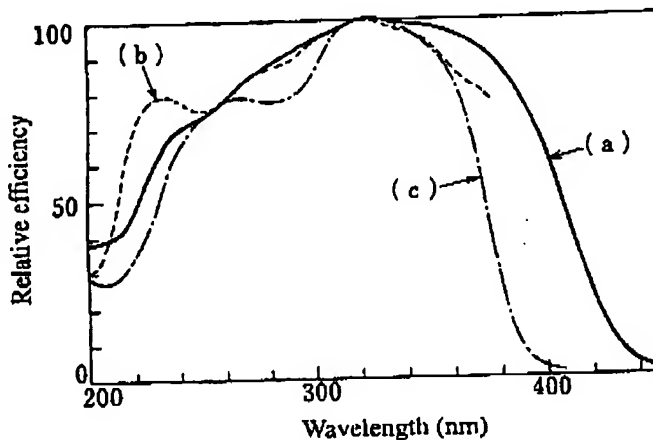


Figure 37 Excitation spectra of (a) $\text{Sr}_2\text{Si}_3\text{O}_8 \cdot 2\text{SrCl}_2 \cdot \text{Eu}^{2+}$; (b) $\text{Ba}_3\text{MgSi}_2\text{O}_8 \cdot \text{Eu}^{2+}$; and (c) $(\text{Sr},\text{Ba})\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{Eu}^{2+}$. (From Kamiya, S. and Mizuno, H., unpublished results. With permission.)

symmetry, while the Ba-feldspar ($\text{BaAl}_2\text{Si}_2\text{O}_8$) has monoclinic symmetry. The Sr-Ba feldspar forms a solid solution up to Sr contents of 40 mol%.^{48,49}

Emission characteristics. The Sr-feldspar phosphor activated by Eu^{2+} shows the strongest emission when 40 mol% Sr^{2+} is replaced by Ba^{2+} . The emission and excitation spectra of $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{Eu}^{2+}$ are shown in Figure 36(c) and 37(c), respectively.

Preparation. Starting materials— SrCO_3 , BaCO_3 , $\alpha\text{-Al}_2\text{O}_3$, and Eu_2O_3 —are mixed in the mole ratio $0.6\text{SrO}:0.4\text{BaO}:\text{Al}_2\text{O}_3:2\text{SiO}_2:0.01\text{Eu}_2\text{O}_3$ with 10 weight% NH_4Cl . The mixture is fired at temperatures of 1150 to 1400°C in a slightly reducing atmosphere, preferably a mixture of 5% hydrogen in nitrogen by volume.

Use. The $\text{Sr}_{0.6}\text{Ba}_{0.4}\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{Eu}^{2+}$ phosphor can be used in diazo photocopying lamps.